Colloid Polym Sci (2006) 284: 733–744
DOI 10.1007/s00396-005-1420-4

ORIGINAL CONTRIBUTION

Rajib K. Mitra
Bidyut K. Paul

Physicochemical investigations of anionic–nonionic mixed surfactant microemulsions in nonaqueous polar solvents: I. Phase behavior

Received: 24 May 2005
Accepted: 1 September 2005

R. K. Mitra · B. K. Paul (✉)
Geological Studies Unit,
Indian Statistical Institute,
203 B.T. Road,
Kolkata 700108, India
e-mail: bidyut@isical.ac.in

Abstract Phase behaviors of AOT/heptane (Hp)/formamide (FA), ethylene glycol (EG), propylene glycol (PG), triethylene glycol (TEG) and glycerol (GLY) have been investigated in the absence and presence of a nonionic surfactant, polyoxyethylene (2) cetyl ether (Brij-52) at 303 K. The phase characteristics of (AOT+Brij-52)/Hp/(EG or PG or TEG) have been found to be different from that of AOT/Hp/FA systems in respect of both the area of monophasic domain and the appearance of other mesophases. The area of monophasic domain of (AOT+Brij-52)/Hp/EG depends on the content of Brij-52 ($X_{\text{Brij-52}}$) and shows a maximum at $X_{\text{Brij-52}}$=0.4. A negligible effect on the area of the monophasic domain has been shown by more hydrophobic surfactants, polyoxyethylene(2) stearyl ether (Brij-72) and polyoxyethylene(2) oleyl ether (Brij-92). The effect of oils (dodecane and hexadecane) on the mixed systems stabilized by (AOT+Brij-52) in EG has been investigated. The area of monophasic domain has been found to be dependent on the type of nonaqueous solvents and follows the order GLY>EG>PG>TG. A systematic investigation on the measurement of phase volumes of mixed surfactant systems [AOT+nonionic surfactant(s)] stabilized in oils of different chain lengths (heptane, dodecane and hexadecane) and polar solvent (EG) has been carried out at different compositions of the ingredients to identify the phase transitions of these systems as a function of $X_{\text{Brij-52}}$. The threshold point of phase transition (both W I→W IV and W IV→W II transitions) has been found to be a function of the configuration of added nonionic surfactant, nature of the polar solvent and oil. The conversion of the initial oil/EG droplets into EG/oil droplets with increasing X_{nonionic} has been facilitated for hydrophobic surfactants polyoxyethylene (4) lauryl ether (Brij-30), Brij-52, and Brij-72 in comparison to the hydrophilic surfactants polyoxyethylene(10) cetyl ether (Brij-56) and polyoxyethylene(20) cetyl ether (Brij-58).

Keywords AOT · Brij-52 · Microemulsion · Mixed surfactant · Nonaqueous polar solvents · Phase behavior · Phase volume

Introduction

Microemulsions are isotropic and thermodynamically stable dispersions of otherwise immiscible liquids like oil and water, wherein the stability is rendered by the monolayer formed by surfactant molecules between the two phases [1]. Due to the microheterogeneous nature of the dispersions, microemulsions find applications in various fields of science, technology and medicine [3, 4]. The dispersions are often found to be structured and formulations containing droplet or bicontinuous structures are frequently encountered. Other structured phases like liquid crystalline, hexagonal, sponge-like, etc., are also found in some cases. The literature on the phase behavior and structural aspects of microemulsion involving substantial amount of oil (hydrocarbon) and water (as polar and aqueous solvent) stabilized by surfactant (s) and/or cosurfactant (generally small chain alcohols) is numerous. However, a few of them are cited herein [2, 5–7].

In recent years, attempts have been made to prepare and study waterless (nonaqueous) microemulsions. Following this purpose, polar solvents having high dielectric constants and low miscibility with hydrocarbon solvents, like formamide (FA), *N*-methyl formamide (NMF), dimethyl formamide (DMF), ethylene glycol (EG), propylene glycol (PG), triethylene glycol (TEG), glycerol (GLY), dimethyl acetamide (DMA), etc., have been used. These nonaqueous microemulsions have attracted attention from both the theoretical (thermodynamics, particle interactions) and practical application points of view [8]. These systems can also be used as novel reaction media in organic reactions like esterification [9] and polymerization [10], and in photophysical studies [11–13]. Nonaqueous systems often show much larger stability regions of isotropic solutions as compared to the analogous aqueous systems [14]. These systems are also interesting due to their application in a large number of fields such as cosmetics, solar energy conversion, semiconductors and microcolloids whose sizes can be controlled by that of the droplets used in their formation and in biological systems [15–17]. The initial reports on microemulsion system, in which water was replaced by polar solvents like GLY, EG and FA and different amides using different surfactants, were due to Fletcher et al. [8], Rico and Lattes [14] and Friberg and Podzinsek [16]. Later Friberg et al. [18–22] published a series of work regarding the formation, phase behavior and structural investigation of microemulsion systems containing nonaqueous polar solvents. They concluded a significant difference between these systems with the corresponding aqueous systems. The aqueous systems were found to be structured, whereas the corresponding nonaqueous systems were less structured and much closer to the structureless solutions. Das et al. [23] reported a similar observation with NMF and DMF with the help of a self-diffusion study. The phase behavior of AOT/FA/heptane and AOT/GLY/heptane has been reported to be similar to those of water-in-oil (w/o) microemulsions [24–26]. Auvray et al. [27] determined the phase behavior and extracted structural information using SAXS measurements of the system CTAB/1-butanol/isooctane/FA. Ward and du Reau [28] reported FA and GLY-based microemulsions and compared the microemulsion regions between these nonaqueous (polar) and aqueous systems.

Schubert et al. [26, 29, 30] and Schubert and Strey [31] reported the phase behavior of microemulsion systems stabilized by FA in the presence of nonionic and ionic amphiphiles stabilized by hydrocarbon oils in the absence and presence of NaBr. Ranieri et al. [32] investigated the phase behavior of water/GLY/TX100 system in a wide range of temperature (5–85°C). Martino and Kaler [33, 34] studied the phase behavior of GLY, PG/hydrocarbon oils (heptane, dodecane, hexadecane)/C_iE_j microemulsions and determined the microstructure with the help of SAXS, SANS and NMR self-diffusion coefficient measurements. Dorfler [35] studied the phase behavior of ternary and quaternary mixtures of water/EG/*n*-dodecane/$C_{14}E_6$. Dorfler and Swaboda [36] reviewed the phase behaviors of a variety of quaternary and ternary systems of the type dodecane/aliphatic alcohols/SDS/water or FA, EG, PG, propylene carbonate, dimethylsulfoxide (DMSO), and acetonitrile. Jonstromer et al. [37] investigated the microemulsion structure using a polar solvent mixture of water and NMF by measuring self-diffusion coefficients with the help of nuclear magnetic resonance Fourier transformation pulsed-gradient spin echo (NMR FT-PGSE) technique. Ray and Moulik [38] studied the phase behavior and transport properties (conductance and viscosity) and thermodynamics of Winsor IV microemulsification of nonaqueous microemulsions formed with polar solvents (FA, EG, PG, DMF and dimethylacetamide)/oils (heptane, isooctane, octane, xylene, and toluene) in the presence of AOT. Mukherjee et al. [39] measured the kinetics of alkaline hydrolysis of crystal violet in aqueous and nonaqueous ethylene glycol microemulsions stabilized with AOT and isooctane. They reported that the rate of the reaction in nonaqueous polar microemulsion exceeded that in the aqueous environment.

In our previous reports [40–46], physicochemical studies of microemulsion/reverse micellar systems stabilized by more than one surfactant using water as the polar solvent have been presented, as the mixed surfactants often show properties superior to those of the individual ones. Studies of microemulsion systems using nonaqueous polar solvents stabilized by more than one surfactant are not reported until this date in the literature. In view of the above, this paper is the first attempt to investigate the phase behavior of microemulsion systems stabilized by mixed anionic (AOT)–nonionic surfactant(s) (specially Brijs of different sizes of polyoxyethylene groups and hydrophobic moieties) with nonaqueous polar solvents (FA, GLY, EG, PG and TEG) of different polarities. The effects of mixing the ratio of the surfactants, size of the polar head group of nonionic surfactants, and chain length of hydrocarbon oil on the phase behavior have been investigated. Phase volume measurements of these systems have been carried out extensively and transition of the phases with increasing nonionic content in the total surfactant concentration has been encountered.

Materials and methods

Materials

Anionic surfactant sodium bis(2-ethylhexyl) sulfosuccinate (AOT, 99%) was a product of Sigma Aldrich, USA. Nonionic surfactants, polyoxyethylene(4) lauryl ether (Brij-30), polyoxyethylene(2) cetyl ether (Brij-52), polyoxyethylene(10) cetyl ether (Brij-56), polyoxyethylene(20) cetyl ether (Brij-58), polyoxyethylene(2) stearyl ether (Brij-72) and polyoxyethylene(2) oleyl ether (Brij-92) were purchased from Fluka, Switzerland. Nonaqueous polar solvents, formamide (FA), ethylene glycol (EG), propylene glycol (PG), triethylene glycol (TEG) and glycerol (GLY) were extrapure AR-grade chemicals of SRL, India. Heptane (Hp), dodecane (Dd) and hexadecane (Hd) were purchased from Fluka, Switzerland. All of these chemicals were used without further purification.

Construction of phase diagrams

At constant temperature, the phase diagram of a ternary system comprising of surfactant, oil and polar solvent can be best represented by a Gibbs triangle with the three components as the apexes. In case of a quaternary system comprising of mixed surfactant (ionic+nonionic), oil and polar solvent, a phase tetrahedral is the best representation of the phase diagram with two surfactants, oil and polar solvent as the four apexes. Such representation can be simplified by keeping the surfactant molar ratio constant and cutting the phase tetrahedral at a constant ionic–nonionic surfactant molar ratio, which results in a simplified Gibbs triangle. The phase diagram in the present study has been constructed using these modified Gibbs triangles. To construct the phase diagrams, oil and surfactant were mixed in different proportions in sealed test tubes, equilibrated at 303 K (if not otherwise specified) in a thermostatic water bath and then titrated with polar solvents using a microsyringe followed by vigorous shaking in a vortex shaker. The appearance of different phases has been identified with naked eyes and the triangular phase diagrams are constructed accordingly. To carry out the phase volume measurements, calculated amounts of surfactant(s), oil and polar solvents were taken in graduated sealed test tubes, shaken vigorously for at least 10–15 min in a vortex shaker, and then kept in a thermostatic water bath at 303 K (if not otherwise specified). The samples were kept for 1 day to ensure complete phase separation and then the phase volumes were noted after inspection through naked eyes.

Results and discussion

Phase behavior

AOT/Brij-52/Hp/FA system

Figure 1a depicts the phase behavior of ternary AOT/Hp/FA system at 303 K constructed in Gibbs triangle with the three components fixed as the three apexes. The phase diagram is characterized by two small microemulsion zones, one along the AOT–Hp axis and the other in the AOT–FA axis. The former region can be assumed to be oil-continuous microemulsion (L_2 phase) containing AOT-coated FA droplets. The FA uptake in this region is very small (≥10% of the total weight). The other region initiates in the 40–60 wt.% of AOT in the AOT–FA axis and extends up to the Hp corner with gradual thinning. The microemulsion region in the vicinity of the AOT/FA axis can be assumed to have surfactant-coated oil droplet structure in FA continuum (L_1 phase). These two microemulsion phases are separated by viscous, gel and turbid phases, which initiate from the Hp corner extending to the AOT corner and expand with increasing weight fraction of AOT. The phase diagrams have been constructed by titration method along the FA-dilution lines wherein FA is added into a mixture of AOT/Hp. Initially, a L_2 phase appears and on further addition of FA, a clear viscous phase is produced. When more FA is added into this system, the formulation becomes turbid. On further addition of FA, a clear gel phase appears. When a few more drops of FA are added into it, the gel phase breaks down and a turbid phase appears which has been found to be low viscous in nature and does not separate into different phases on long standing. All these phases have been found to be thermodynamically stable in nature and their formation is reproduced by titration along the oil-dilution line. The existence of mesophases at high-AOT-concentration region in AOT/Hp/FA has been reported earlier by Ray and Moulik [38]. The gel phase is separated from the viscous and L_1 phases by two turbid phase channels. A wide biphasic zone is produced along the FA–Hp axis, which extends up to 50 wt.% of AOT. In the present study, the occurrence of small L_2 region may be due to the poor solubilization of FA as compared to that of water in the AOT/Hp system [47, 48].

The phase behavior of the pseudo-ternary system AOT/Brij-52/Hp/FA at 303 K is represented in Fig. 1b, wherein the mole fraction of Brij-52 ($X_{\text{Brij-52}}$) in total surfactant is fixed at 0.2 and the surfactant mixture (AOT+Brij-52) has been assumed to be a single component [41, 42]. It has been observed that both L_1 and L_2 regions have increased in size with respect to the AOT system, whereas that of the biphasic region has diminished. The turbid phase between the viscous and gel phase regions has shrunk considerably providing space for wider L_2 and viscous phases. $X_{\text{Brij-52}}$ is

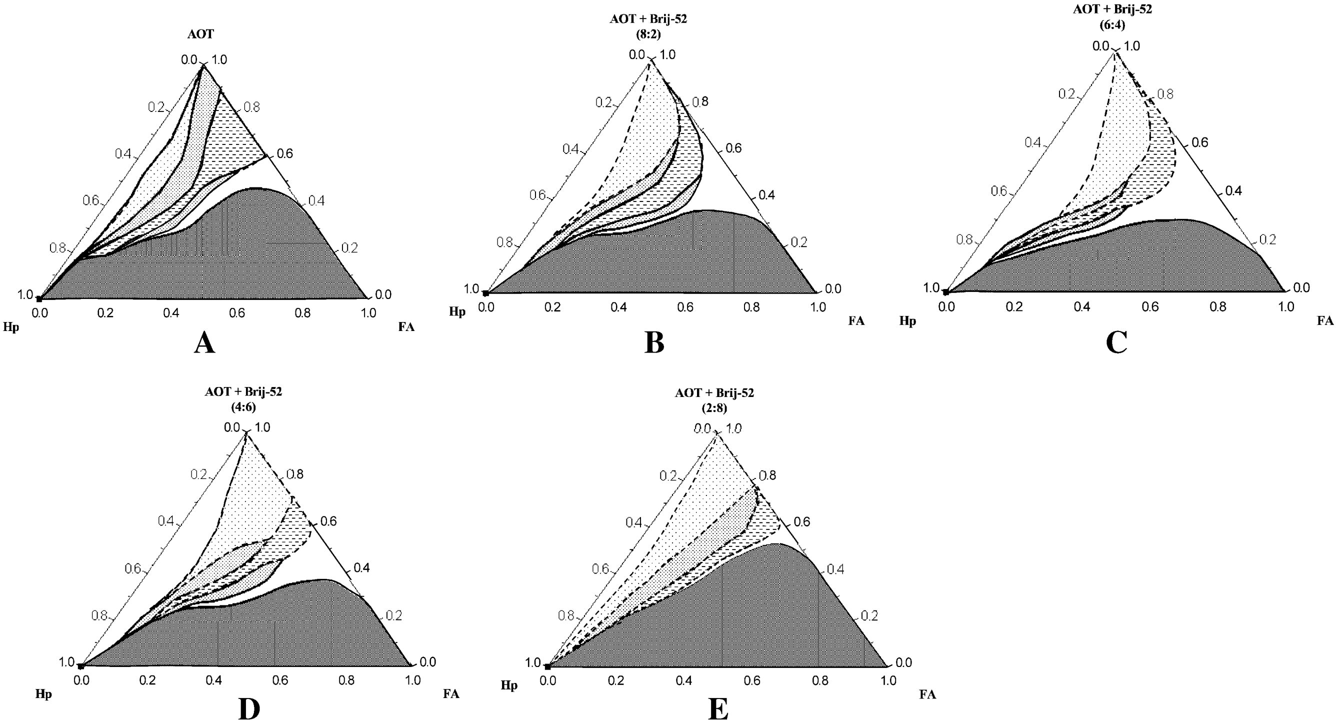

Fig. 1 Triangular phase diagram of the system AOT/Brij-52/Hp/FA at 303 K in five different mole fractions of Brij-52 (**a** 0, **b** 0.2, **c** 0.4, **d** 0.6, and **e** 0.8). The *clear zone* indicates the microemulsion domain. The other regions characterized are (▩) biphasic region, (▒) viscous region, (▤) gel region, (▦) and turbid region

further increased to 0.4 and the phase diagram of the mixed system is depicted in Fig. 1c. In this mixed system, a wider L_2 phase with a correspondingly small biphasic region is produced. Both of the turbid phases have been squeezed noticeably. On further increase of the Brij-52 content to $X_{\text{Brij-52}}$=0.6, the L_2 region gets reduced and the biphasic region gets enlarged compared to the earlier system ($X_{\text{Brij-52}}$=0.4) (Fig. 1d). The turbid regions are also enlarged with a subsequent decrease of the gel phase. The L_1 phase is reduced only marginally. At a higher Brij-52 content ($X_{\text{Brij-52}}$=0.8), a large biphasic region is produced with substantially small L_2 and L_1 regions (Fig. 1e). The turbid region occurring between the viscous and gel phases is increased and extends up to the surfactant–FA axis, whereas that occurring between the gel and L_1 phase disappears. The increase in extent of L_2 region up to $X_{\text{Brij-52}}$=0.4 may be due to the synergism in water solubilization capacity of w/o microemulsions in the presence of mixed surfactant systems as reported earlier [44, 45].

AOT/Brij-52/Hp (or Dd or Hd)/EG (or PG or TEG or GLY)

Figure 2 depicts the phase diagram of AOT/Brij-52/Hp/EG system at 303 K at five different mole fractions of Brij-52 ($X_{\text{Brij-52}}$=0, 0.2, 0.4, 0.6 and 0.8). The phase behavior of AOT-stabilized system ($X_{\text{Brij-52}}$=0) is characterized by the presence of a symmetrically shaped large monophasic microemulsion region and a biphasic region at the low-surfactant-concentration region along the Hp–EG axis. Unlike the FA system, no mesophase like viscous, gel or turbid phases appear in these systems. A narrow viscous phase appears in the high-surfactant-concentration region, which has not been shown in the figure. When Brij-52 is blended with AOT at $X_{\text{Brij-52}}$=0.2, a larger monophasic domain is produced in comparison to the AOT system. On further increase of $X_{\text{Brij-52}}$ to 0.4, the area of the monophasic domain increases further, and an equal weight percent of Hp and FA can be microemulsified using ~20% surfactant. When $X_{\text{Brij-52}}$ is increased to 0.6, the monophasic region is reduced in comparison to the previous system ($X_{\text{Brij-52}}$=0.4), particularly in the EG-rich region. At $X_{\text{Brij-52}}$=0.8, the area of monophasic region is reduced considerably and the monophasic region produced is smaller than that obtained with the AOT system. To understand the effect of configuration of the hydrophilic moiety of the nonionic surfactant on the phase characteristics, AOT–nonionic blends using Brij-72 and Brij-92 have also been studied. A similar trend in the phase behavior has been observed as was observed in the case of Brij-52 systems (figures not shown). The fraction of the area of microemulsion region in the total phase diagram has been plotted as a function of the mole faction of Brij-52 (or Brij-72 or Brij-92) in surfactant mixture and is depicted in Fig. 3. It is evident from the figure that the microemulsion

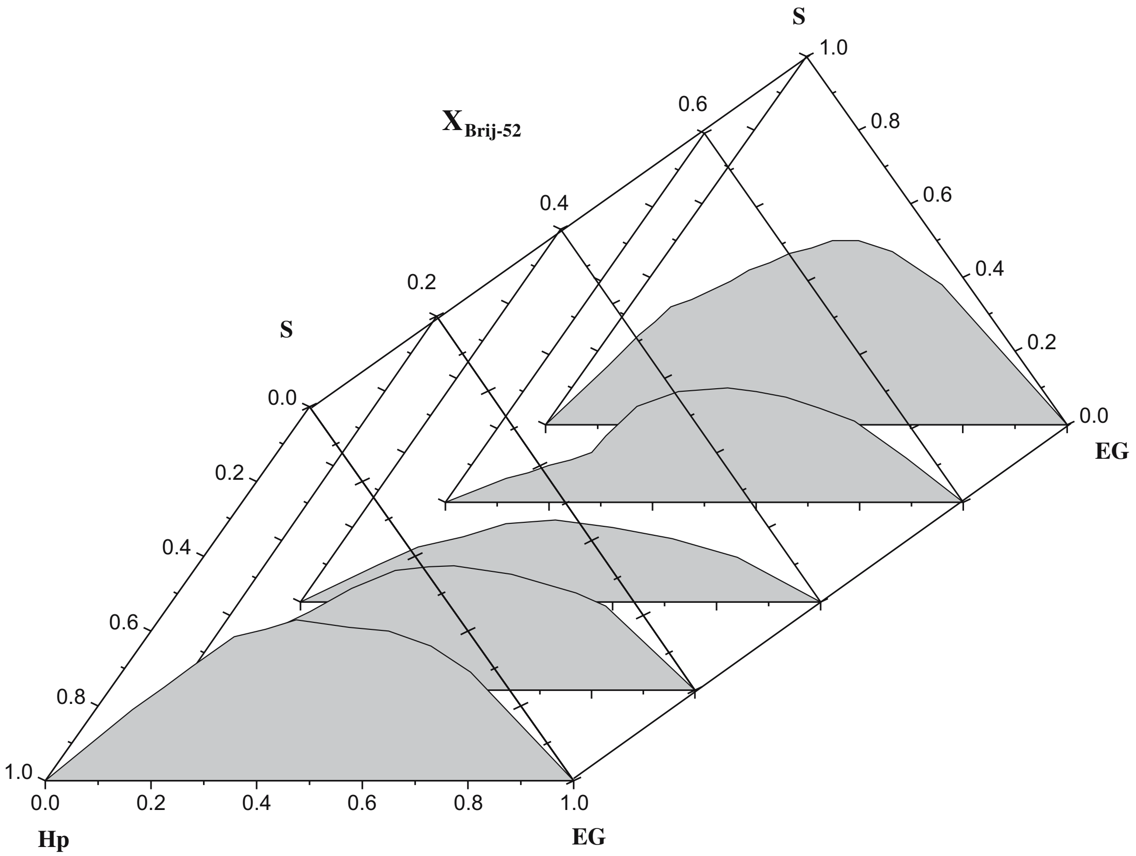

Fig. 2 Triangular phase diagram of the system AOT/Brij-52/Hp/EG at 303 K in five different mole fractions of Brij-52 (0, 0.2, 0.4, 0.6, 0.8). The *clear zone* indicates the microemulsion domain

region increases up to X_{Brij}=0.4 and then decreases with an increase in X_{Brij}. The area of microemulsion zone differs only marginally for these systems and follows the order Brij-52~Brij-72>Brij-92.

The phase separation in a microemulsion system is primarily governed by two opposing effects, namely, the curvature of the droplets and the interdroplet interaction. When the two effects counterbalances each other, large solubilization is obtained [46, 49]. In the present study, the increase in solubilization with increasing $X_{\mathrm{Brij\text{-}52}}$ can be assumed to be due to the increase in the droplet size. But increasing droplet size also induces a stronger interdroplet interaction, which brings in phase separation. When the two effects are optimized, the largest monophasic domain is obtained (as at X_{Brij}=0.4 in AOT/Brij-52/Hp/EG system). It is found that the area of monophasic domain is poorly dependent on the head group size of the nonionic surfactants (Fig. 3). It has been reported that the increase in droplet size is proportional to the head group area of the surfactant [50]; hence, identical effects on phase characteristics are produced by all these systems.

The phase behavior of AOT/Brij-52/Dd/EG is depicted in Fig. 4. The monophasic area of the AOT-stabilized system is less than that obtained with Hp. When Brij-52 is blended with AOT, the monophasic zone increases monotonically, specially in the oil-rich region. Phase behavior of this mixed system is also carried out with Hd

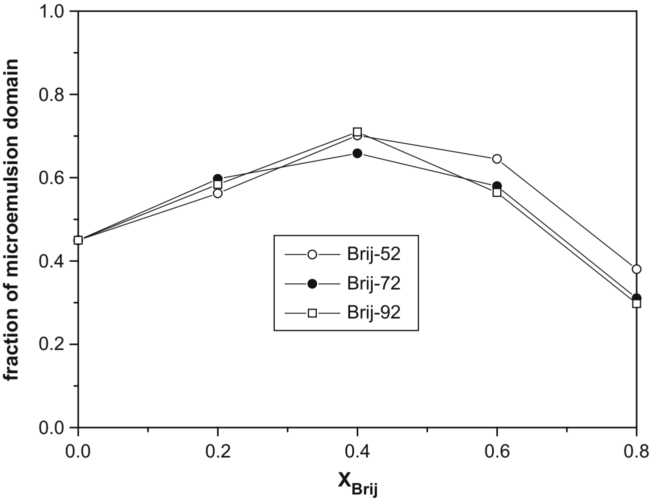

Fig. 3 Fraction of microemulsion domain in the total phase diagram of the system AOT/Brij-52 (or Brij-72 or Brij-92)/Hp/EG as a function of X_{Brij} at 303 K

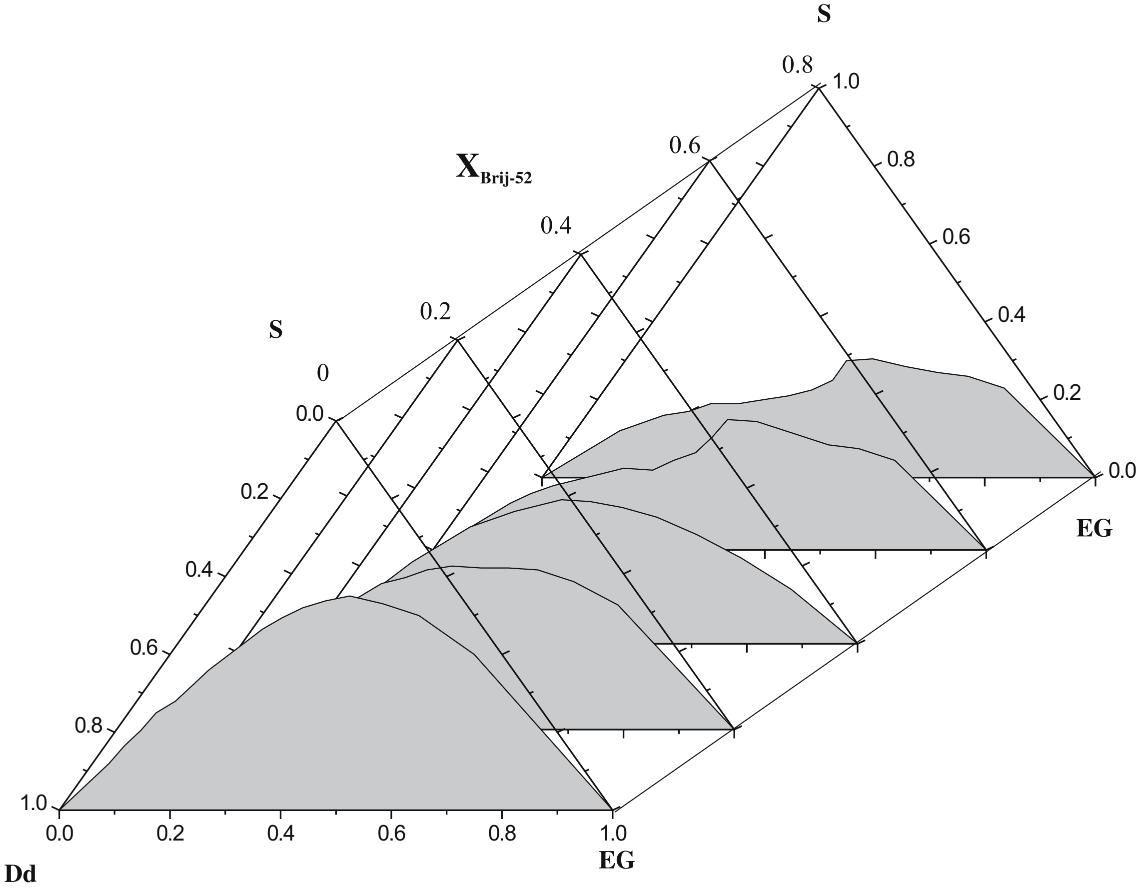

Fig. 4 Triangular phase diagram of the system AOT/Brij-52/Dd/EG at 303 K in five different mole fractions of Brij-52 (0, 0.2, 0.4, 0.6, 0.8). The *clear zone* indicates the microemulsion domain

oil (not exemplified). In this system, solubilization increases with increasing $X_{\text{Brij-52}}$ up to 0.6, beyond which it decreases. The relative area of microemulsion with these three oils has been plotted in Fig. 5. It is found that up to $X_{\text{Brij-52}}$=0.4, the area of microemulsion area follows the order Hp>Dd>Hd. At $X_{\text{Brij-52}}$=0.6, the three systems have almost identical microemulsion areas. The Hd system reaches a maximum in solubilization capacity at $X_{\text{Brij-52}}$=0.6. At $X_{\text{Brij-52}}$=0.8, the Dd system has the largest solubilization capacity followed by Hd and Hp.

The AOT/Hp/EG-stabilized system produces larger microemulsion domains than the Dd- and Hd-stabilized systems. This could be explained in the following manner: Oil penetration into the interfacial layer plays an important role in determining phase separation in these systems, specially for oil-continuous inverted micellar systems [49]. When such droplets coalesce, oil molecules are removed from the interface and the larger is the chain length of hydrocarbon, the higher is its probability to get removed from the interface and, hence, the smaller is the microemulsion region formed. It has been reported earlier that in AOT/water in hydrocarbon oil microemulsion systems, the solubilization capacity of water is maximum with Hp and

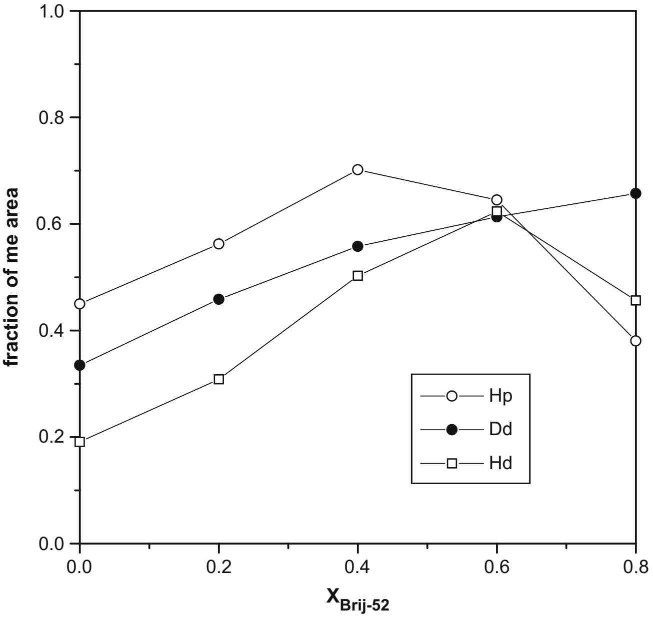

Fig. 5 Fraction of microemulsion domain in the total phase diagram of the system AOT/Brij-52/Hp (or Dd or Hd)/EG as a function of $X_{\text{Brij-52}}$ at 303 K

then falls off regularly with increasing chain length of hydrocarbons [49]. We have found earlier that the same trend is followed by AOT/hydrocarbon reverse micelles with FA and EG (Mitra and Paul, unpublished). For the mixed systems, replacement of AOT by Brij-52 at the interface increases the droplet radius but it perhaps also supports oil penetration and delays phase separation. The penetrability of Dd reaches an optimum value and thus the extent of monophasic domain increases with increasing $X_{\text{Brij-52}}$ for the entire domain of the studied range of $X_{\text{Brij-52}}$, specially in the oil-rich region.

Phase behavior of AOT/Brij-52/Hp/PG system at 303 K is more or less identical with that of the EG system, and a maximum in solubilization capacity is obtained with $X_{\text{Brij-52}}$=0.4 (figure not shown). For the AOT/Brij-52/Hp/TEG system, solubilization capacity increases with increasing Brij-52 content in the mixture, and the maximum microemulsion zone is obtained at $X_{\text{Brij-52}}$=0.6 (figure not shown), which is higher than that obtained with PG. A large monophasic zone is produced for the system AOT/Hp/GLY (figure not shown). When Brij-52 is blended with AOT at $X_{\text{Brij-52}}$=0.2, the area of the monophasic region increases significantly. But on further addition of Brij-52 into the mixture (at $X_{\text{Brij-52}}$=0.4), the area of the monophasic zone is decreased sharply and has an area less than that obtained with the single AOT system. On increasing the Brij-52 content up to 0.6 and 0.8, the monophasic area is decreased further and only small areas of single-phasic region are obtained. The relative areas of microemulsion region for these four nonaqueous polar systems (EG, PG, TEG and GLY) are presented in Fig. 6. It is evident from the figure that the area of single-phase region for single surfactant (AOT)-stabilized system follows the order GLY> EG~ PG> TEG, but it increases with an increase in the content of the nonionic surfactant ($X_{\text{Brij-52}}$) and follows a maximum, depending on the type of polar solvents. The maximum occurs at different values of $X_{\text{Brij-52}}$ (i.e. 0.2, 0.4, 0.6 and 0.6 for GLY, EG, PG and TEG respectively). The polarity of these nonaqueous solvents decreases in the order GLY>EG>PG>TEG. In the AOT-stabilized system, the extent of microemulsion region also follows the same order. With increasing Brij-52 content, the surfactant mixture becomes more hydrophobic and thus loses the compatibility with GLY and the extent of monophasic domain decreases.

Phase volume measurements

Figure 7a–d illustrate the phase volume profile of the system AOT/Brij-52/Hp/EG at four different compositions of surfactant(s)/Hp/EG (*w*/*w*/*w*): (a) 35/32.5/32.5, (b) 30/35/35, (c) 25/37.5/37.5 and (d) 20/40/40, respectively, with varying $X_{\text{Brij-52}}$ at 303 K. It can be observed from the figure that at $X_{\text{Brij-52}}$=0, i.e. with single AOT system, a large homogeneous phase at the bottom remains in equilibrium with a relatively smaller volume of homogeneous phase. When a polar-solvent-soluble dye eosin blue (EB) is added into this system, the upper phase remains colorless, whereas the lower phase turns intensely violet. On the other hand, upon addition of an oil-soluble dye Sudan-IV, both of the phases turn red. It is evidenced from this dye solubilization experiment that both the phases contain oil, whereas the polar solvent is confined only in the lower phase. Hence, the formulation can be inferred as a Winsor I (W I) system in which an EG-continuous microemulsion with surfactant-coated oil droplets remain in equilibrium with an upper oil phase. The surfactant molecules are distributed in the bulk oil phase and the oil–EG interface inside the microemulsion. When $X_{\text{Brij-52}}$ is increased in the surfactant mixture, the volume fraction of the microemulsion phase increases gradually and eventually at a certain value of $X_{\text{Brij-52}}$, all the excess oil phase gets solubilized and a homogeneous single-phase microemulsion is formed [Winsor IV (W IV) system]. On further increase of $X_{\text{Brij-52}}$, again a biphasic formulation appears wherein a large volume of homogeneous liquid phase remains in equilibrium with a smaller volume of liquid phase at the bottom. It is observed from the dye solubilization experiment that the addition of EB turns the upper phase violet and the lower phase intensely violet, whereas Sudan-IV turns the upper phase red while keeping the lower phase colorless. This indicates that the upper phase is an oil-continuous EG/oil microemulsion in equilibrium with excess EG at the bottom [Winsor II (W II) system]. AOT molecules form a monolayer between oil and EG that bends around the oil phase in order to form AOT micelles in EG that solubilize oil molecules into its interior and the excess oil is ejected out as a separate phase. With increasing $X_{\text{Brij-52}}$, the lipophilicity of the mixed interface

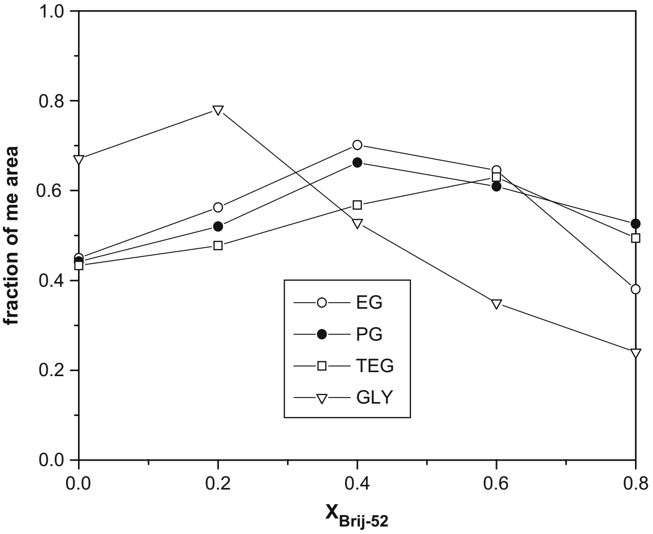

Fig. 6 Fraction of microemulsion domain in the total phase diagram of the system AOT/Brij-52 /Hp /EG (or PG or TEG) as a function of $X_{\text{Brij-52}}$ at 303 K

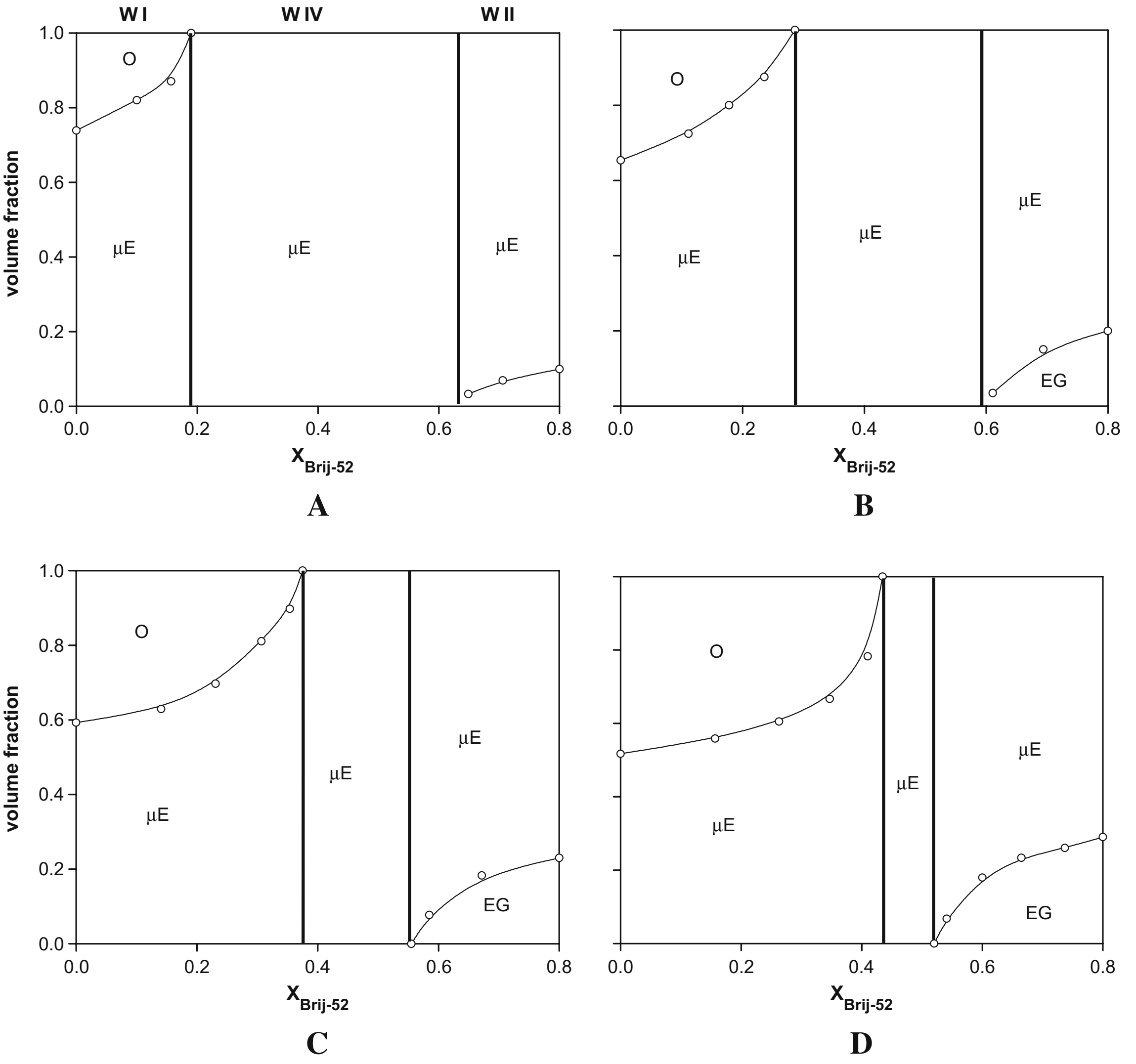

Fig. 7 Volume fraction of the system AOT/Brij-52/Hp/EG at 303 K as a function of $X_{\mathrm{Brij-52}}$ with four different compositions of surfactant/oil/EG (*w*/*w*/*w*): **a** 35/32.5/32.5, **b** 30/35/35, **c** 25/37.5/37.5 and **d** 20/40/40. *W I*, *W II* and *W IV* represents Winsor I, II and IV systems, respectively. *μE*, *O* and *EG* represents microemulsion, oil and EG phases, respectively

increases as it contains a small polar head group (two EO chains) and a large hydrophobic moiety (of 16 carbon atoms). Thus, more oil molecules are solubilized into the micelles and the volume fraction of the microemulsion phase increases with a consequent decrease of the excess oil phase volume as $X_{\mathrm{Brij-52}}$ is increased. At a certain $X_{\mathrm{Brij-52}}$, the interface becomes sufficiently lipophilic and can swell up all the excess oil and a monophasic W IV system is produced. With further increase in $X_{\mathrm{Brij-52}}$, the lipophilicity of the interface increases further and, at a certain $X_{\mathrm{Brij-52}}$, the system becomes too lipophilic to solubilize the total volume of polar solvent. The excess volume of polar solvent is ejected as a separate phase and a W II system is formed. The transition from W I to W II manifests the flipping of surfactant monolayer from normal to inverted micelles, i.e. from a positive curvature to a negative curvature. Such a transition may involve the formation of either a W IV or a Winsor III (W III) system [51]. It has been reported that when the lipophilicity and hydrophilicity of the surfactant(s) is balanced, a three-phase microemulsion is formed and the surfactant attains its maximum solubilization capacity. At this point, the microemulsion has a bicontinuous structure and the microemulsion phase coexists with excess oil and water phases [52]. In the present study, only the W IV system is encountered and no three-phase system is formed. This indicates that the microemulsion phase (W IV) may have the droplet structure.

It can be observed from the figure that with increase in *S* (weight percentage of total surfactant), the W I→W IV and W IV→W II transitions occur at lower and higher $X_{\mathrm{Brij-52}}$ values, respectively, and the homogeneous single-phase microemulsion region is produced over a wider range of

$X_{\text{Brij-52}}$. Increase in S also increases the droplet density [32] and thus the excess oil phase can be solubilized more efficiently.

Phase volume studies have also been carried out on both oil- and EG-rich regions of the phase diagram at compositions S/O/EG (w/w/w); 30/50/20 and 30/20/50, respectively (figures not shown). It is observed that W I→W IV→W II transitions are registered as a function of $X_{\text{Brij-52}}$ for both of these systems. For the oil-rich system, the W I system has been found to contain more or less identical volume of microemulsion phase with that of the equal oil–EG system. But the W I→W IV transition initiates at a lower $X_{\text{Brij-52}}$ value (0.22) than the previous system (0.286). The W IV→W II transition starts up at a higher $X_{\text{Brij-52}}$ value (0.65) and has a relatively smaller volume of the lower excess EG phase. On the other hand, for the EG-rich systems, the W I→W IV transition starts up at a comparable $X_{\text{Brij-52}}$ value (0.23) as that of the Hp-rich system, but the W IV→W II transition initiates at a lower value of $X_{\text{Brij-52}}$ (0.58) in comparison to the previous two systems. The W I systems have larger volume fraction of the microemulsion phase and the W II system have larger volume fraction of the excess EG phase in comparison to the other two systems. At a fixed weight percentage of total surfactant (S=30%), the range of $X_{\text{Brij-52}}$ over which the W IV region exists follows the order, EG-rich system>oil-rich system>equal weight percent of oil–EG system.

To ascertain the effect of the oil chain length on phase volume, three different oils, Hp, Dd and Hd, have been used to study the phase volume of the system AOT/Brij-52/oil/EG at 303 K at three different compositions of S/O/EG (w/w/w) of 30/20/50, 30/35/35 and 30/50/ 20. The results are depicted in Fig. 8a–c. It is evidenced from the figure that with increasing chain length of hydrocarbon oils, the W I→W IV transition occurs at higher $X_{\text{Brij-52}}$ values. The volume fraction of the microemulsion phase also decreases with an increase in the chain length of oil, and the effect is found to be more pronounced for the oil-rich systems. The extent of microemulsion region also decreases with increasing oil chain length. This observation corroborates well with the assumption that the W I microemulsion system consists of surfactant-coated oil droplets in EG continuum. AOT normal micelles in polar solvent EG can be assumed to be not closely packed aggregates due to the strong head group repulsion and a relatively less densely packed hydrocarbon core is formed, which cannot solubilize the whole amount of oil into it. It can be argued that hydrocarbons with higher chain length finds lesser space at the hydrocarbon core of the AOT micelles in EG to get dissolved and, hence, are ejected as an excess phase. Replacement of AOT with Brij-52 increases the lipophilicity of the interface. As the nonionic surfactant is supposed to reside at the interface, it decreases the re-

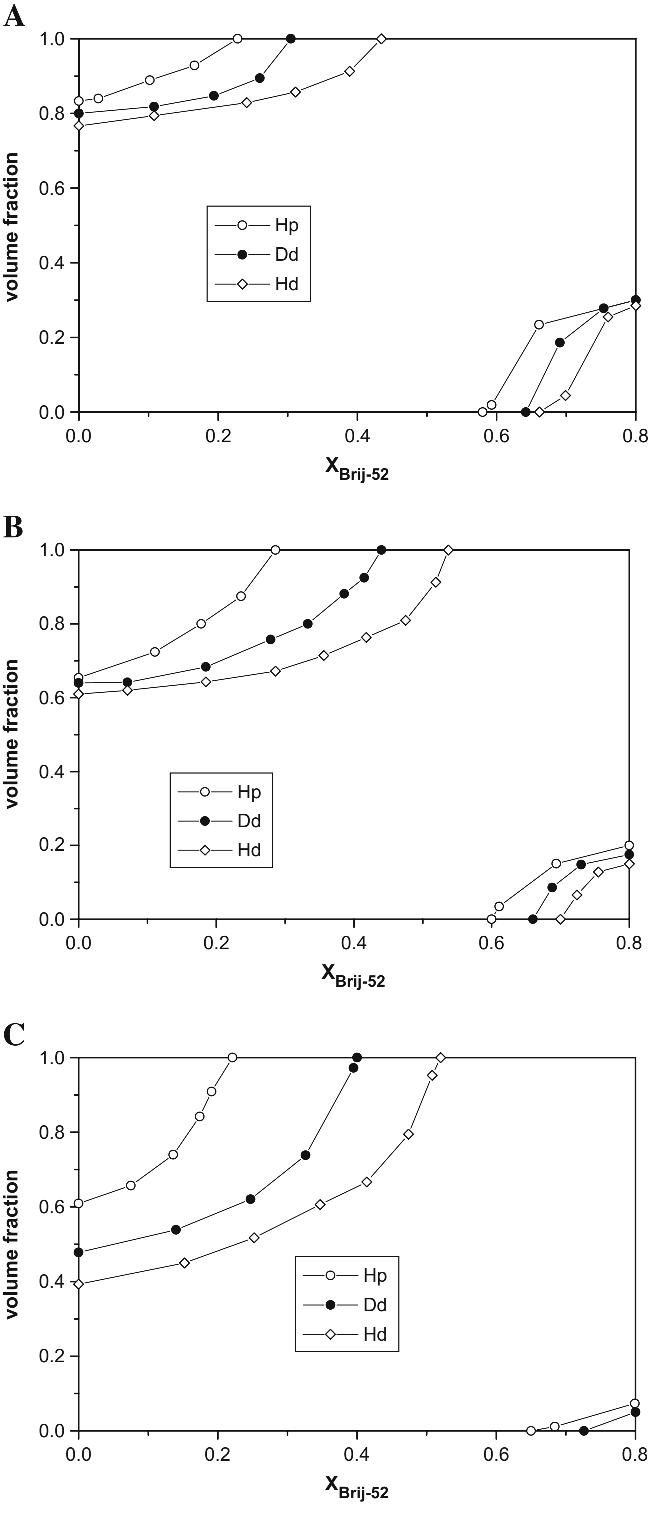

Fig. 8 Volume fraction of the system AOT/Brij-52/Hp (or Dd or Hd)/EG at 303 K as a function of $X_{\text{Brij-52}}$. The compositions of surfactant/oil/EG (w/w/w) are **a** 30/20/50, **b** 30/35/35 and **c** 30/50/20

pulsion among the charged head groups of AOT and thereby makes the micelles more closely packed. This perhaps increases the solubilization of the excess oil phase in the micellar interior, and eventually at a certain $X_{\text{Brij-52}}$ value, the configuration of the micellar interface and core becomes such that all the excess oil molecules get dissolved into it. It can be seen that with increasing hydrocarbon chain length, the $X_{\text{Brij-52}}$ required for the W I→W IV transition shifts to a higher value. This indicates that the larger hydrocarbon finds it difficult to get accommodated in the micellar core and in the interface region. Hence, more Brij-52 at the interface is required to solubilize the excess oil phase. With increasing Brij-52 content, the droplet structure gets inverted into a reverse micellar type. The higher the lipophilicity of the oil, the more Brij-52 at the interface is required to make the interface lipophilic to eject the excess polar phase. Thus, the W I→W IV transition occurs at higher $X_{\text{Brij-52}}$ for long-chain hydrocarbons as evidenced in Fig. 8.

To underline the effect of the configuration (i.e. size of the polar head group and hydrophobic moiety) of the nonionic surfactant on the phase transition, Brij-52 is replaced by different nonionic surfactants (Brij-56, Brij-58, Brij-72 and Brij-30). Phase volume measurements are carried out as a function of X_{nonionic} for the systems AOT/nonionic(s)/Hp/EG at a fixed composition of *S*/*O*/EG 30/35/35 (*w*/*w*/*w*) at 303 K and the results are depicted in Fig. 9. The figure shows that the phase volume does not change appreciably with $X_{\text{Brij-58}}$ for the AOT/Brij-58 mixture and the system remains biphasic for the entire range of studied $X_{\text{Brij-58}}$. For the AOT/Brij-56 mixed system, the volume of the microemulsion phase increases slowly with increasing $X_{\text{Brij-56}}$ and a W I→W IV transition is registered at a high value of $X_{\text{Brij-56}}$ (0.72). No W IV→W II transition is produced within the studied range. On the other hand, the AOT/Brij-72 system produced W I→W IV transition earlier than that of the AOT/Brij-52 system (0.195 as compared to 0.221) and, also, the W IV→W II transition occurs at a lower $X_{\text{Brij-72}}$ (0.63 as compared to 0.646). The blend AOT/Brij-30 exhibits W I→W IV transition at $X_{\text{Brij-30}}$ of 0.424 and W IV→W II transition at 0.707. Brij-56 is more hydrophilic than Brij-52. Due to the presence of a larger polar head group (ten EO chains), the interfacial packing of Brij-56 is not rigid and, hence, only a small amount of oil can be accommodated in the interface and inside the core of the AOT/Brij-56 normal micelles. Also, the decreased hydrophobicity of the interface incorporated upon the addition of Brij-56 instead of Brij-52 indulges lesser oil solubilization at a fixed X_{Brij}. Brij-58 has 20 EO chains, and thus is more hydrophilic in comparison to both Brij-52 and Brij-56 and does not produce any W I→W IV transition within the experimental range, which indicates least amount of oil solubilization for the AOT/Brij-58 mixed system. The appearance of a transition threshold for the Brij-30 system in between that of Brij-52 and Brij-56 confirms this argument. Brij-30 contains a lauryl chain and four EO groups and thus is less hydrophilic than Brij-56 but more hydrophilic than Brij-52. So, at a fixed X_{Brij}, the interface made up of AOT/Brij-30 can solubilize more oil in comparison to that of the corresponding AOT/Brij-56 system, but lesser amount of oil in comparison to the AOT/Brij-52 system. Brij-72 has an equal number of EO chains as that of Brij-52, but possesses two more methylene groups. Thus, the oil solubilization capacity of the AOT/Brij-72 interface can be assumed to be more efficient than the corresponding AOT/Brij-52 interface, and it is found that the W I→W IV transition occurs at a lower X_{Brij} for the former blend.

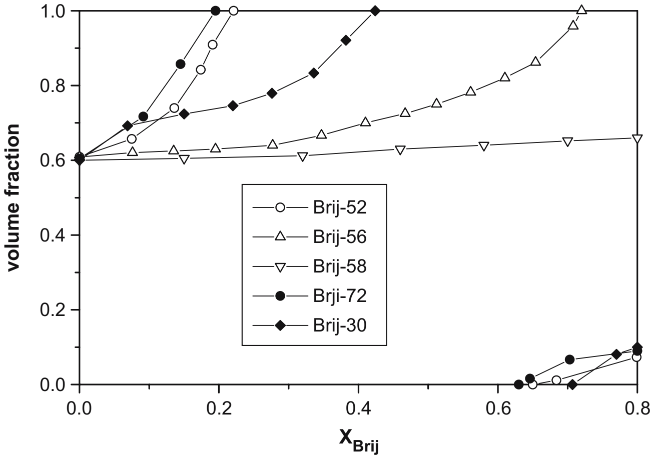

Fig. 9 Volume fraction of the system AOT/Brij-52 (or Brij-56 or Brij-58 or Brij-30 or Brij-72)/Hp/EG at 303 K as a function of $X_{\text{Brij-52}}$ with surfactant/oil/polar solvent (*w*/*w*/*w*) composition of 30/35/35

Phase volume measurements of the mixed system AOT/Brji-52/Hp in the presence of three structurally different glycols, EG, PG and TEG show W I→W IV→W II phase transition for all the systems (figure not shown). It is further observed that the W I→W IV transition takes place at different threshold values of $X_{\text{Brij-52,}}$ and follows the order EG<PG<TEG. On the other hand, the W IV→W II is only poorly dependent on the nature of the nonaqueous solvent as the transition thresholds are closely spaced and follows the order EG~PG<TEG. These results can be explained in the light of micellar behavior of surfactants in polar medium. It is known that the monomeric solubility of surfactants in the polar solvents like EG, PG, and TEG is higher in comparison to that in water, and the cmc of different surfactants in these polar solvents is higher than that in water. It can be argued that since the monomeric solubility of the hydrophobic surfactant, Brij-52, in polar solvents follows the order EG<PG<TEG, thus the availability of Brij-52 at the interface follows the order EG>PG>TEG. Consequently, the threshold $X_{\text{Brij-52}}$ required for the solubilization of the excess oil phase follows the order EG<PG<TEG.

To determine the effect of temperature on the phase transition of these mixed systems, phase volume measurements are carried out at a temperature range of 283–333 K with the system AOT/Brij-52/Hp/EG at a fixed composition of *S*/*O*/EG 30/35/35 (*w*/*w*/*w*) at five different $X_{\text{Brij-52}}$ (0, 0.1, 0.2, 0.8 and 1.0) (figure not shown). It is found that the phase volume has a negligible dependence on temperature over the studied range of temperatures for all these systems. Both W I ($X_{\text{Brij-52}}$=0, 0.1 and 0.2) and W II ($X_{\text{Brij-52}}$=0.8, 1.0) systems have shown little change in the volume fraction of microemulsion phase with increasing temperature. The mixed systems with $X_{\text{Brij-52}}$ values in the range of 0.3 to 0.7 have been found to be monophasic within the entire experimental range.

Conclusions

The phase diagram of AOT/Brij-52/Hp/FA is characterized by the presence of a small monophasic region and a large biphasic region along with mesophases like viscous, gel and turbid phases, whereas that stabilized by other nonaqueous solvents (EG, PG, TEG and GLY) is characterized by large monophasic regions. The extent of monophasic domain of AOT/Brij-52/Hp/EG first increases and then decreases with an increase in content of Brij-52 ($X_{\text{Brij-52}}$) after passing through a maximum (at $X_{\text{Brij-52,max}}$=0.4). Replacing Brij-52 with Brij-72 and Brij-92 produces negligible effect on the extent of the monophasic domain. The area of monophasic region increases with $X_{\text{Brij-52}}$ for the dodecane system, while the hexadecane system produces the maximum at $X_{\text{Brij-52}}$=0.8. The extent of monophasic domain is also a function of the nonaqueous polar solvents used and follows the order GLY>EG>PG>TEG. Phase volume measurements of AOT/Brij-52/Hp/EG at a constant composition of *S*/*O*/EG as a function of $X_{\text{Brij-52}}$ has produced a typical W I→W IV→W II phase transition with increasing X_{Brij}. The threshold point of phase transition (both W I→W IV and W IV→W II transitions) has been found to be a function of the configuration of added nonionic surfactant, nature of the polar solvent and oil. The conversion of the initial oil/EG droplets into EG/oil droplets with increasing X_{Brij} is facilitated for hydrophobic surfactants (Brij-30, Brij-52, and Brij-72) in comparison to the hydrophilic surfactants (Brij-56 and Brij-58). The results have been explained in the light of monomeric solubility of surfactants in the polar solvents and hydrophobicity of the nonionic surfactants.

Acknowledgement The authority of Indian Statistical Institute, Kolkata is acknowledged for financial support in the form of a project and a senior research fellowship to RKM.

References

1. Moulik SP, Paul BK (1998) Adv Colloid Interface Sci 78:99
2. Paul BK, Moulik SP (1997) J Dispers Sci Technol 20:301
3. Paul BK, Moulik SP (2001) Curr Sci 80:990
4. Solans C, Kunieda H (eds) (1997) Industrial applications of microemulsions. Marcel Dekker Inc, NY
5. Sjoblom S, Lindberg R, Friberg SE (1996) Adv Colloid Interface Sci 95:125
6. Eastoe J, Robinson BH, Steytler DC, Thorn-Leeson D (1991) Adv Colloid Interface Sci 35:1
7. De TK, Maitra AN (1995) Adv Colloid Interface Sci 59:95
8. Fletcher PDI, Galal M, Robinson BH (1984) J Chem Soc Faraday Trans I 80:3307
9. Fletcher PDI, Freedman RB, Robinson BH, Rees GD, Schomacker R (1987) Biochim Biophys Acta 912:278
10. Schubert KV, Lusvardi KM, Kaler EW (1996) Colloid Polym Sci 274:875
11. Riter RE, Kimmel JR, Undiks EP, Levinger NE (1997) J Phys Chem B 101:8292
12. Falcone RD, Correa NM, Biasutti MA, Silber JJ (2000) Langmuir 16:3070
13. Silber JJ, Falcone RD, Correa NM, Biasutti MA, Abuin E, Lissi E, Campodonico P (2003) Langmuir 19:2067
14. Rico I, Lattes A (1984) J Colloid Interface Sci 102:285
15. Lopez-Cornejo P, Costa SMB (1998) Langmuir 14:2042
16. Friberg SE, Podzinsek M (1984) Colloid Polym Sci 262:252
17. Bergstom K, Holmberg K (1992) Colloids Surf 63:273
18. Friberg SE, Whon CS (1985) Colloid Polym Sci 263:156
19. Friberg SE, Liang YC (1986) Colloid Polym Sci 264:449
20. Friberg SE, Liang YC (1987) Colloids Surf 24:325
21. Friberg SE, Liang YC (1987) In: Friberg SE, Bothorel P (eds) Microemulsions: structure dynamics, CRC, Boca Raton, Florida
22. Friberg SE, Rong G (1988) Langmuir 4:796
23. Das KP, Ceglie A, Lindman B (1987) J Phys Chem 91:2938
24. Bergenstahl B, Jonsson A, Sjoblom J, Stenius P, Warnheim T (1987) Prog Colloid &Polym Sci 74:108
25. Schubert KV, Strey R, Kahlweit M (1992) Prog Colloid Polym Sci 89:263
26. Schubert KV, Busse G, Strey R, Kahlweit M (1993) J Phys Chem 97:248
27. Auvray X, Petipas C, Anthore R, Rico I, Lattes A, Ahmend-Zadeh Samii A, de Savignac A (1987) Colloid Polym Sci 265:925
28. Ward AJI, du Reau C (1993) In: Matijevic E (ed) Surface and colloid science, vol 15, Plenum, NY, pp 153–196
29. Schubert KV, Strey R, Kahlweit M (1992) In: SH Chen et al (eds) Structure and dynamics of strongly interacting colloidal and supramolecular aggregates in solution, Kluwer, The Netherlands, p 841
30. Schubert KV, Strey R, Kahlweit M (1992) In: SE Friberg, B Lindman (eds) Organized solutions, Marcel Deker, NY p 105
31. Schubert KV, Strey R (1991) J Chem Phys 95:8532
32. Ranieri GA, Coppola L, Terenzi M, Mesa CL (1994) Ber Bunsenges Phys Chem 98:603
33. Martino A, Kaler EW (1990) J Phys Chem 94:1627
34. Martino A, Kaler EW (1995) Langmuir 11:779

35. Dorfler HD (1998) Prog Colloid Polym Sci 109:118
36. Dorfler HD, Swaboda C (1993) Colloid Polym Sci 271:586
37. Jonstromer M, Olsson U, Parker WO (1995) Langmuir 11:61
38. Ray S, Moulik SP (1994) Langmuir 10:2511
39. Mukherjee L, Mitra N, Bhattacharya PK, Moulik SP (1995) Langmuir 11:2866
40. Mitra RK, Paul BK (2003) J Surf Sci Technol 19:139
41. Mitra RK, Paul BK (2004) J Surf Sci Technol 20:105
42. Mitra RK, Paul BK (2005) J Colloid Interface Sci 283:565
43. Mitra RK, Paul BK (2005) Colloids Surf A 252:243
44. Mitra RK, Paul BK (2005) Colloids Surf A 255:165
45. Paul BK, Mitra RK (2005) J Colloid Interface Sci 288:261
46. Mitra RK, Paul BK (2005) J Colloid Interface Sci 291:550
47. Riter RE, Kimmel JR, Undiks EP, Levinger NE (1997) J Phys Chem B 101:8292
48. Riter RE, Undiks EP, Kimmel JR, Levinger NE (1998) J Phys Chem B 102:7931
49. Hou MJ, Shah DO (1987) Langmuir 3:1086
50. Moulik SP, Ray S (1994) Pure Appl Chem 62:521
51. ML Robbins (1976) “Theory of the Phase Behavior of Microemulsions” In: KL Mittal (ed), Micelllization, Solubilization, and Microemulsions, Vol 2, Plenum, NY, p 713
52. Pes MA, Kunieda H (1995) Trends Phys Chem 5:75